The Nuclear Properties of Gold

THE APPLICATIONS OF ITS ISOTOPES IN MEDICINE AND IN INDUSTRY

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Gold has in all twenty-four radioisotopes, although only two of them have half-lives which make them suitable, in combination with the normal chemical inertness of gold, for use in clinical work or in industrial research and control. Their production methods and some of their most important applications in these fields are described.

Radioisotopes are isotopes in which the nuclei of the atoms contain either more or fewer neutrons than are present in the naturally occurring stable iostopes of the elements. Such nuclei are unstable, and they tend in time to change into stable configurations by radioactive decay. The primary radioactive decay process is always either the emission of a charged particle (an alpha particle, a positron or a beta particle), or the capture by the nucleus of an orbital electron. These processes change the charge on the nucleus, yielding a nucleus which is chemically a different element. The product nucleus has a lower energy content than the parent radioactive nucleus; the difference in energy appears as the energy of various kinds of radiations which are emitted.

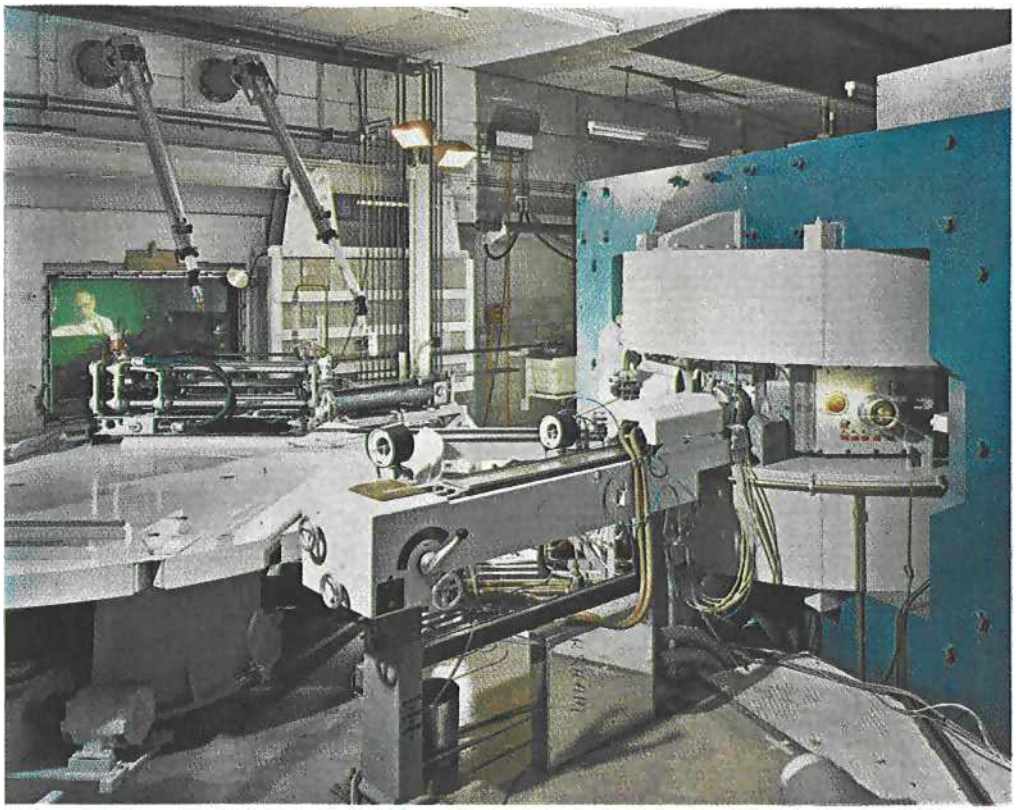
These radiations consist of charged particles accompanied in many cases by electro-magnetic radiation in the form of gamma-rays. It is the properties of the charged particles and electro-magnetic radiations and the fact that radioisotopes are chemically indistinguishable from stable isotopes of the same element which give rise to their varied applications. For example, the therapeutic uses of radiosiotopes depend on the ability of the radiations to ionise atoms of the substances through which they pass; this ionisation in turn leads to chemical and biological changes. The ease of detection and measurement of the radiations are responsible for the uses of radioisotopes in medical diagnosis and for the enormous variety of tracer applications in research and technology.

Gold has an atomic number of 79 and an atomic weight of 196.967. The atom of the only stable isotope, ^{197}Au, thus has a nucleus containing 79 protons and 118 neutrons, with 79 orbital electrons, but in all twenty-four radioisotopes have been identified, several of them exhibiting metastable as well as ground states. For the record, details of these are given in the table with their half-lives and

The Isotopes of Gold

Mass Number	Half Life	Mode of Decay: Alpha Particle	Electron Capture	Positron Emission	Beta Particle	Gamma Photons
177	1.35 sec	x				
178	2.65 sec	x				
179	7.25 sec	x				
181	11.55 sec	x	x			
183	45.5 sec	x				
185	4.3 min	x	x			
186	12 min		x			x
187	8 min	x	x			
188	8 min		x			x
189	29.7 min		x			x
189m	4.7 min		x			x
190	39 min		x			x
191	3.2 hour		x			x
192	5.0 hour		x	x		x
193m	3.9 sec					x
193	17.5 hour		x			x
194	39.5 hour		x	x		x
195m	31.00 sec			x		x
195	183 day		x			x
196m	9.7 hour					x
196	6.2 day		x		x	x
197m	7.5 sec					x
197	STABLE					
198	2.70 day				x	x
199	3.15 day				x	x
200	48.4 min				x	x
201	26 min				x	x
202	30 sec				x	x
203	55 sec				x	x
204	4.05 sec				x	x

m=metastable, a nuclear isomer with energy above that of the ground state.



The cyclotron at the Radiochemical Centre at Amersham, capable of accelerating positively charged particles to above 20 MeV for the production of isotopes deficient in neutrons. This is equipped with a specially designed remotely controlled target-changing arrangements to avoid delays in its use. Here the target head is being attached to the rotating target assembly by manipulators

emissions, but of this lengthy list only two have significant applications.

In common with other heavy elements the neutron-deficient radioisotopes made by bombarding lighter atoms with positively charged particles in a cyclotron or a linear accelerator fall into two distinct groups. Nuclides with mass numbers from 177 to 183 are pure alpha emitters, all with half-lives of less than one minute, while those with mass numbers of 185 to 196, which decay by electron capture accompanied by gamma radiations (and in some cases by positron emission), are also short lived with the exception only of ^{195}Au with a half-life of 183 days. The remainder, the neutron-heavy isotopes made by neutron-capture reactions, follow the normal pattern of beta decay accompanied by gamma photons of medium energy. Nuclides in this latter group also have short half-lives, ranging from only a few seconds to three days.

The Production of Isotopes

The production of isotopes in a cyclotron is achieved by bombarding a target with positively charged particles; these may be protons (hydrogen nuclei) of mass 1 and charge 1, deuterons (heavy hydrogen nuclei) of mass 2 and charge 1, or in exceptional cases alpha particles (helium nuclei) of mass 4 and charge 2.

The following nuclear reactions, indicating the addition of one or more protons to the nucleus followed by the loss of neutrons are typical:

$$^{192}_{78}\mathrm{Pt} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{192}_{79}\mathrm{Au} + 2\,{}^{1}_{0}\mathrm{n}$$

$$^{193}_{77}\mathrm{Ir} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{194}_{79}\mathrm{Au} + 3\,{}^{1}_{0}\mathrm{n}$$

$$^{195}_{78}\mathrm{Pt} + {}^{1}_{1}\mathrm{p} \rightarrow {}^{195}_{79}\mathrm{Au} + {}^{1}_{0}\mathrm{n}$$

The only radioisotope of gold having a reasonably long half-life is ^{195}Au. This is prepared by bombarding a target of natural platinum with 22 MeV protons. Although the abundance of ^{195}Pt in natural platinum is only 33.8 per cent, little advantage would be gained by using an enriched target because the radioisotopes of gold that are formed from the other four stable isotopes of platinum have half-lives very much shorter than that of ^{195}Au.

The process involves the sole use of a cyclotron—a very expensive piece of equipment—followed by meticulous radiochemical work, the gold being separated from platinum and any impurities either

Nuclear Properties of ^{195}Au and ^{198}Au

Mass Number	Half Life	Radiation Energies in MeV		
		Beta	Gamma	Characteristic X-ray
195	183 days	—	0.031 0.099 0.130 0.210	0.067 (Pt)
198	2.7 days	0.29 0.96 1.37	0.412 0.676 1.088	0.07 (Hg)

by solvent extraction or by cation exchange. Consequently the cost of this product is high, around £75 per millicurie. The yield from a thick platinum target varies between 0.4 and 1.7 millicuries per hour with a beam current of 100 microamp.

The most common radioisotope of gold is made by a neutron capture reaction in a nuclear reactor:

$$^{197}_{79}\text{Au} + ^{1}_{0}\text{n} \rightarrow ^{198}_{79}\text{Au}$$

The reaction is a particularly favourable one, for two reasons. Not only is the target material, metallic gold, both chemically and physically stable and also readily available in a high state of purity, but the high cross-section of the neutron capture reaction—98.8 barns—enables a useful specific activity to be achieved for clinical purposes in a nuclear reactor of quite moderate power. For example, with a neutron flux of 2×10^{13}n/cm^2/s the specific activity reaches 1 curie per gram in 6.5 hours or 77 curies per gram in 65 hours.

The secondary reaction

$$^{198}_{79}\text{Au} + ^{1}_{0}\text{n} \rightarrow ^{199}_{79}\text{Au}$$

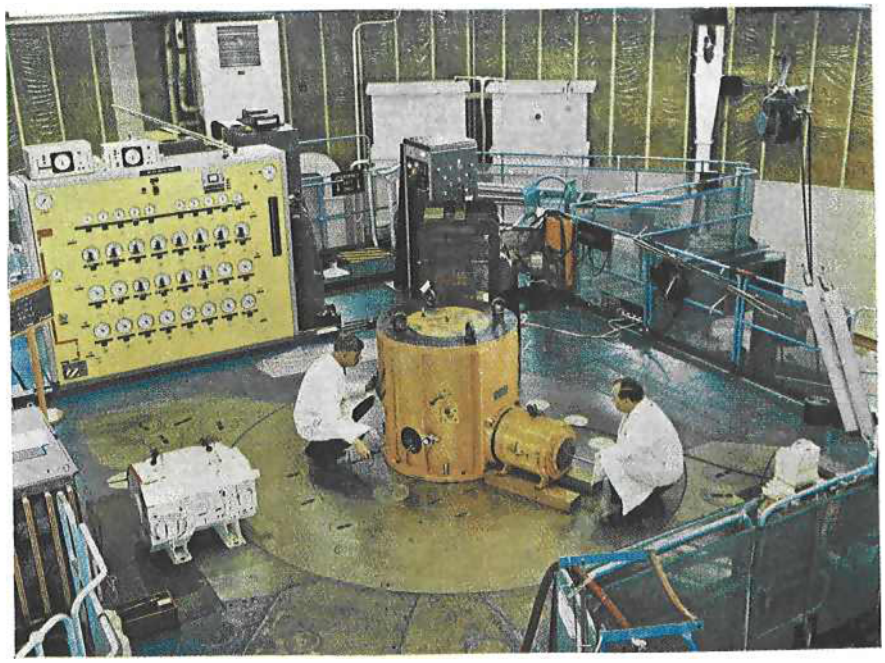
significant because of its very high cross-section, about 20,000 barns, introduces a small proportion of ^{199}Au with a half-life of 3.15 days and with rather less energetic beta and gamma emissions.

Details of these two isotopes and their emission energies are set out in the table alongside.

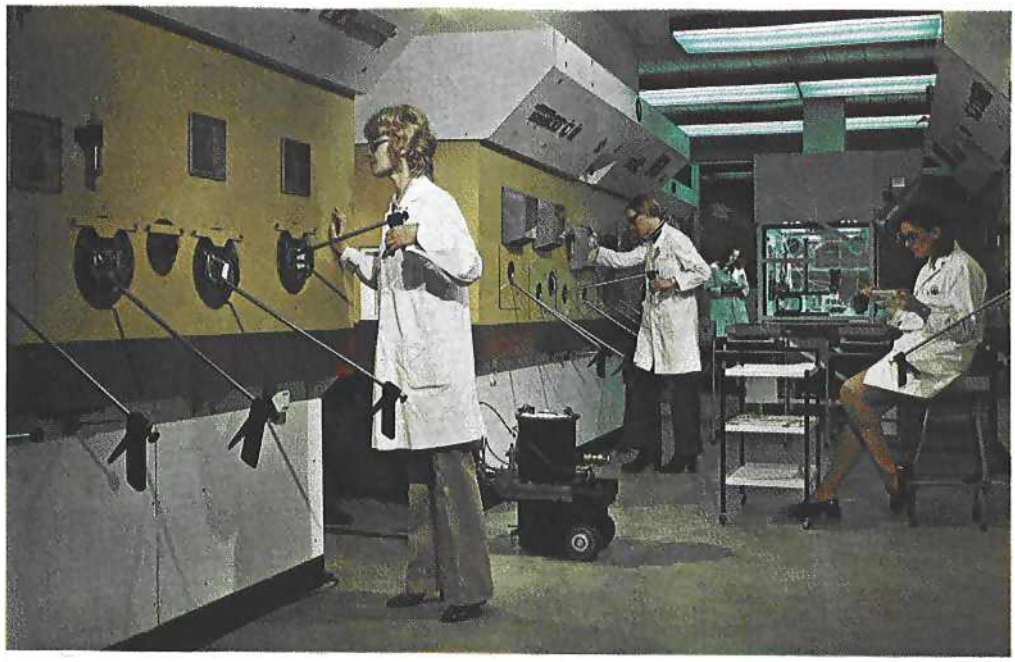
Therapeutic Applications

The radioisotopes of gold are used predominantly in medicine for both therapy and diagnosis. ^{198}Au is made as a matter of routine for clinical use in most developed countries, the annual output in the United Kingdom being around 5 kilocuries, while world production is probably of the order of 150 kilocuries annually. This is a much less expensive product, the price as gold colloid injection being about 70 pence per millicurie.

Radiation sources of ^{198}Au in the form of implants known as "gold grains" are used extensively in the treatment of malignancies and have replaced over the past twenty years or so the so-called radon seeds formerly used for the same function.



The experimental high flux nuclear reactor PLUTO at Harwell, and other similar reactors, are fitted with special mechanisms for loading and unloading targets for irradiation by neutron bombardment



Following irradiation careful radiochemical work is necessary to separate the isotope from impurities. In this shielded and ventilated enclosure at the Radiochemical Centre, one of many such units designed for chemical operations carried out by remote control, gold injections are being sterilised and packaged

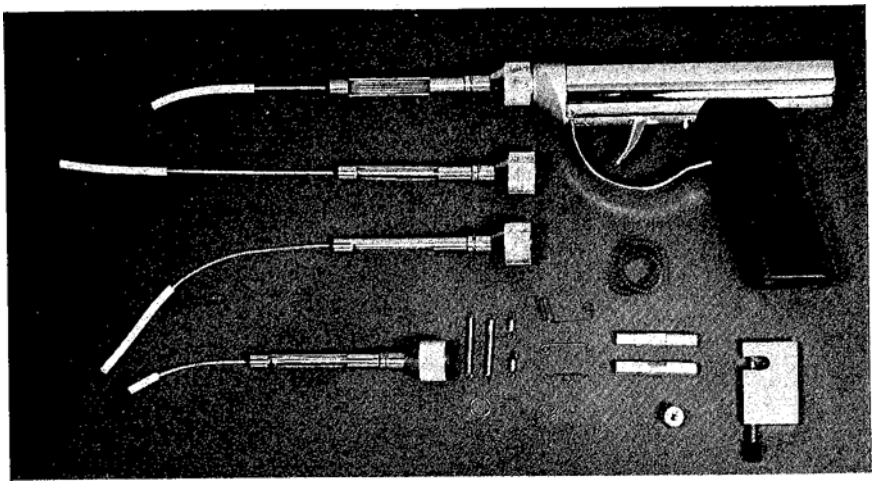
In the early days of radiotherapy—say from 1920 until 1950—many treatment centres maintained equipment for collecting and purifying the emanation from a solution containing 1 to 5 grams of radium as chloride. A measured activity of this gas (a mixture of nitrogen and radon) was then introduced into a length of glass capillary tube, which was drawn out in a flame and sub-divided into "seeds" about 5 mm long and 0.7 mm in diameter containing 1 to 5 millicuries of radon. These radon seeds emitted gamma radiation derived from the decay products of radon, with an effective half-life of the parent nuclide, 3.83 days, but they also emitted beta radiation of high energy (up to 3.2 MeV from the disintegration product ^{214}Bi). Because this high beta dose would have been delivered to tissue in immediate contact with the seeds, they were employed clinically after encapsulation in platinum tubes of 0.5 mm wall thickness, sufficient to absorb the beta radiation.

The radiological hazards to operators making these glass seeds were difficult to control and in the late 1940s an improved pattern of radon seed was introduced in the United States and was speedily adopted in many other countries. Advantage was taken of two properties of gold in the form of annealed tubing—its high density coupled with the ability to cut it with a tool of appropriate contour and at the same time to seal the cut ends by cold welding. Thus a length of gold tube 1.35 mm diameter and wall thickness 0.5 mm, filled with a mixture of nitrogen and radon, could be sub-divided reliably and accurately by a remotely controlled mechanism, while the high density of gold served to absorb the unwanted beta radiation, reduced the radiological hazards to the operators and rendered the platinum sheath unnecessary.

This technique, in the days when only naturally occurring radioisotopes were available, enabled the radiation from a limited quantity of expensive radium to be utilised in a more flexible and more economical way than would have been the case were the radium used to fill sealed sources such as needles or tubes, and the system is still operated in some parts of the world.

A radon plant is completely self-supporting, but its operation demands specialised skill and knowledge. As more and more nuclear reactors have been built, and the rapid distribution of short-lived radioisotopes by air freight has been organised, so radon seeds have gradually been displaced by the "grains" of ^{198}Au, these having similar applications with several practical advantages.

The gold grain in most common use comprises a small cylinder of pure gold, 2.2 mm long and 0.5 mm diameter, enclosed in platinum of 0.15 mm thickness to absorb the beta radiation—of much lower energy than that from ^{222}Rn—forming a cylinder of overall dimensions 2.5 mm in length by 0.8 mm diameter. Implants in the body are made via a cannula using an implantation gun—the model designed at the Royal Marsden Hospital in London is an outstandingly successful example—which



Radioactive gold grains are inserted in the required site in a patient's body by means of an implantation gun. Designed by the Royal Marsden Hospital and made by the Medical Supply Association, the gun has four different types of needles, and the grains can be delivered to the site without further handling

accepts aluminium magazines holding 14 gold grains. These magazines, filled with inactive grains, are irradiated in a nuclear reactor; after allowing the short-lived radioisotopes formed in the aluminium of the magazine and in the platinum sheathing to decay, the activity in gold is measured and the grains are distributed with a certificate of measurement. The United Kingdom output of activated grains is about 30,000 annually; inactive gold grains made in Britain are exported to many countries in the Commonwealth and in Europe for activation there.

Gold grains are implanted in the treatment of tumours on many sites, particularly in the lips and mouth. The illustration is a radiograph showing an array of gold grains implanted in the tongue of a patient at the Hammersmith Hospital, London.

Colloidal Gold Injection

A protected colloidal solution of ^{198}Au has wide applications in both therapy and diagnosis and is the subject of monographs in pharmacopoeias in many countries. In therapy, colloidal gold is used in effect as a liquid beta emitter; the chemical inertness of metallic gold combined with the short half-life of ^{198}Au make it highly suitable for this application.

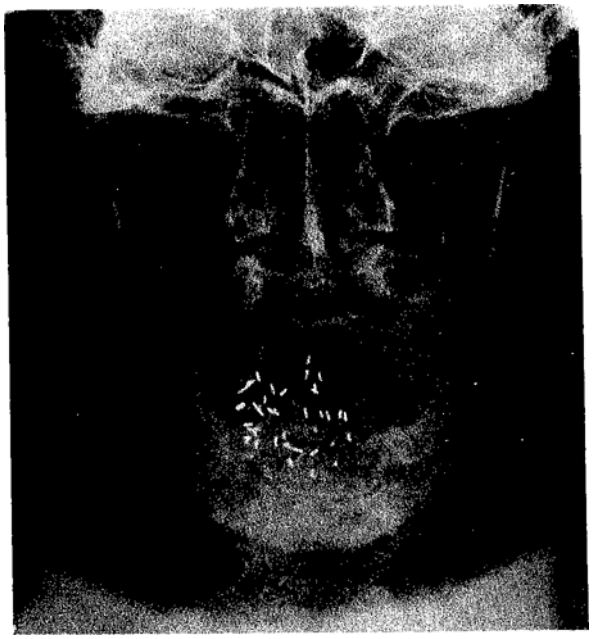
To produce this preparation a pure gold target is irradiated in a nuclear reactor for two to three hours—the short period of radiation restricts the formation of ^{199}Au—in a flux of $2 \times 10^{14} n/cm^2/s$, dissolved to yield $HAuCl_4$, and reduced with dextrose and sodium hydroxide in the presence of gelatine as a protecting agent. The particle size of the colloid is controlled by the experimental conditions; two types are in common use, one with a wide spectrum up to 20 millimicrons and the other, produced by a more refined seeding technique, with a restricted range of particle sizes, mainly 20 to 30 millimicrons. These preparations are sufficiently stable to allow sterilisation by heating in an autoclave at 120°C.

The injection, containing 20 to 100 millicuries ^{198}Au, per millilitre is used intravenously, interstitially and in particular intracavitarly in the pleural and peritoneal cavities.

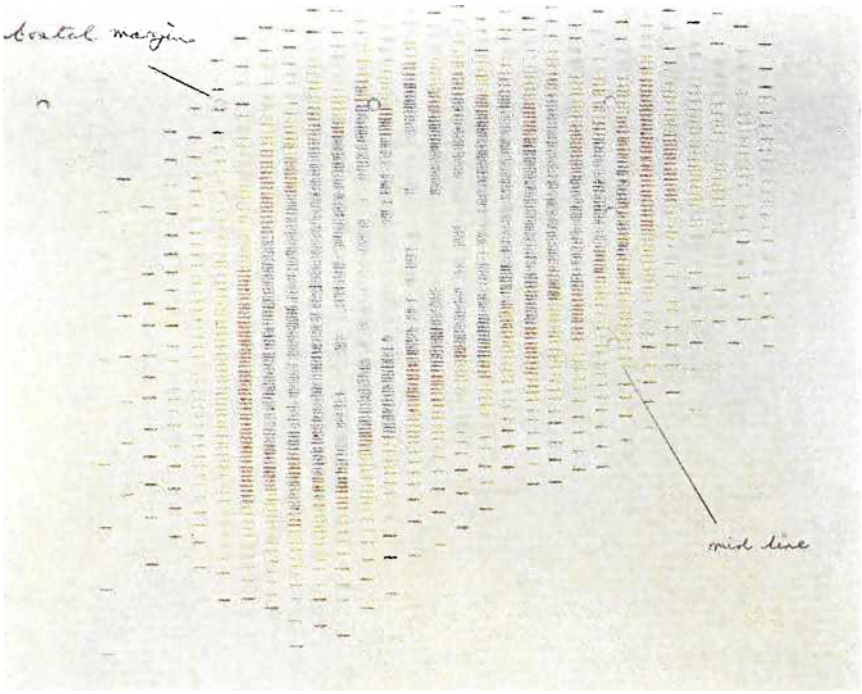
Another and quite different application is in the treatment of chronic effusion of the knee joint resulting from rheumatoid or degenerative arthritis. Injections of colloidal gold have been found to give successful results in some 60 per cent of patients treated.

Diagnostic Technique

A fast growing diagnostic technique is the method of visualising organs within the body by scintigraphy. A tracer amount of a short-lived gamma emitting radioisotope, i.e. a quantity too small to have any



A radiograph showing the treatment of a carcinoma in the floor of the mouth with radioactive gold grains. They may be removed after treatment or left permanently in place until they become inactive



A scintigram taken of a patient's liver at St Bartholomew's Hospital, London. The technique involves the introduction into the organ of a small amount of radioactive gold and then plotting its distribution with a gamma ray camera

significant effect on the patient's metabolism but sufficient to be detected from outside the body by sensitive instruments, is introduced into the organ and its distribution is observed from without the body. This can be done either by scanning the body surface adjoining the internal organ with a sodium iodide crystal probe of small cross sectional area and plotting the results or alternatively by using a gamma camera, an instrument which records an "image" of the organ. Either method with refined electronic instrumentation produces a two dimensional visualisation of the organ and indicates areas of malfunction.

In the majority of diagnoses, the radioisotope is injected in the form of a radioactively labelled chemical which is taken up selectively by the organ suspected to be diseased. For example, the kidneys can be visualised using the diuretic drug chlormerodrin $NH_2CONHCH_2CH(OCH_3)CH_2HgCl$ labelled with ^{197}Hg. ^{198}Au in colloidal suspension is not of course selectively absorbed, but it finds considerable use in delineating the lungs and liver by scintigraphy. The illustration shows a scintigram of a liver made with colloidal ^{198}Au at St Bartholomew's Hospital in London.

Applications in Research and Technology

The applications of the radioisotopes of gold are less numerous in the industrial and technical sphere than their medical uses, but a number of interesting techniques have been established.

The high cross-section of the neutron capture reaction and the convenient gamma emission make the determination of gold at very low concentrations by activation analysis followed by radiochemical separation on carrier (e.g. by solvent extraction of $HAuCl_4$ with $CH_3COOC_2H_5$) particularly favourable. The technique has been applied, for example, to the analysis of iron meteorites collected from many sites in the United States, giving values between 0.1 and 3.7 parts per million, and to determining the gold content of marine organisms including seaweeds, molluscs, crustacea and fish as well as sea water (which was found to contain about 0.00003 parts per million of gold).

The sensitivity of this new technique enables results of acceptable precision to be obtained on smaller samples in a much shorter time than by using spectrometric methods.

The short half-life and the convenient gamma energy has also indicated the use of ^{198}Au as a tracer in studies on the solidification of large steel ingots. A tracer is added at several stages during the solidification period; sections are then taken and the distribution of check tracer visualised by autoradiography. This technique has demonstrated the rate of movement of the solidification front in the interior of the ingot and has suggested further studies into the causes of heterogeneity.

Similarly, in the continuous casting of steel ingots a knowledge of skin formation has been obtained by the use of ^{198}Au tracers and has improved the casting operation. The isotope is added to the molten steel

and after the slabs have solidified samples are cut and ground and the activity measured.

A technique in which ^{198}Au is used to trace sediment movement in the sea has recently been adopted in South Africa in the study of harbour development. The gold tracer is attached to a sand sample by chemical exchange with silver previously deposited on to the sample by a chemical silvering process.

At the test site the radioactive sand is mixed with a sediment slurry in a lead shielded pot, which is lowered to the sea bed and emptied by remote control from the deck. The labelled sand particles are transported by the sea movements and their dispersal can then be traced by means of a sensitive gamma detector towed across the sea bed. This technique has two important advantages over a fluorescent tracer technique previously employed; the tracer material can be readily identified and the dispersion of sediment can be observed directly and correlated with data on winds and tide movements.

In the laboratory the 67 KeV K X-ray from a source of ^{195}Au has been used in X-ray fluorescence spectrometry, but this application is restricted by the high cost and comparatively short half-life of the nuclide.

The transitions of ^{195}Au which generate 98.8 and 129 KeV gamma rays exhibit the Mössbauer effect. This has been used in studies of the physical and chemical structure of metallic platinum and its alloys, of intermetallic compounds and of oxides and halides.

Gold Alloy Spark Plug Electrodes

EASIER STARTING AND LONGER LIFE

To perform its function efficiently a spark plug must maintain a gap spacing that will satisfy engine operation over the full range of output from idling to full throttle, achieve this with minimum fuel consumption, and resist the effects of both electrical erosion and chemical attack from the products of combustion.

A very great deal of research has gone into the design and development of the spark plug to meet modern conditions of motoring. One recent development, by Champion Spark Plug of Toledo, Ohio, is the introduction of a range of plugs with centre electrodes tipped with gold alloy wire. These spark plugs, although somewhat more expensive, have been enthusiastically adopted in such applications as snowmobiles and motorcycles where fast and sure starting is required even in sub-zero weather conditions.

The use of the gold alloy electrode – a 60 per cent gold 40 per cent palladium alloy – offers a number of advantages in engine performance, including easier starting and less gap erosion. Easier starting results from reduced voltage required to fire the plug. In addition, since the small size of the electrode means that more spark is exposed to the fuel charge than with standard electrodes, the gap size can be reduced, which again lowers the voltage demand on the ignition system.

The outstanding resistance to corrosion of the gold-palladium alloy has made it possible to design these plugs with a smaller diameter insulator tip, allowing greater clearance between the insulator and the shell at the firing end. This results in better scavenging of fuel deposits and, as a consequence, better protection from fouling. Similarly the marked decrease in gap erosion observed with these plugs is attributable to the much greater resistance of the gold alloy to the atmosphere in the combustion chamber by comparison with the more conventional electrode materials.

The centre electrode of this Champion spark plug in a gold-palladium alloy is specifically designed to provide ease of starting even in extremely cold weather conditions, while the high resistance to corrosion of the gold alloy ensures a longer service life than can be expected with plugs fitted with conventional electrodes